ELECTROCHEMICAL STUDIES OF SOME COORDINATION COMPOUNDS OF IRON

BY

WARD BEECHER SCHAAP

B.S., Wheaton College, 1944
M.S., University of Illinois, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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UNIVERSITY OF ILLINOIS, 1950

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ELECTROCHEMICAL STUDIES OF SOME COORDINATION COMPOUNDS OF IRON

Electrochemical data were obtained by means of the polarograph to study the complexes that the divalent and trivalent ions of iron form in solution with the anions of the homologous series of dicarboxylic acids, oxalic, malonic and succinic. For those oxidation-reduction reactions that occur reversibly at the dropping mercury electrode, information can be obtained regarding the formulas and stabilities of the oxidized and reduced species and the standard potentials of the systems (1).

In potassium oxalate solutions ranging in concentration from 0.003 to 0.95 molar, and containing 0.001 molar iron(III) added as the perchlorate, the polarographic waves obtained corresponded to reversible, one-electron reduction of the trioxalatoferrate(III) ion to two different iron(II) complex ions. In solutions containing more than 0.2 molar oxalate ion, the reduction proceeds to the trioxalatoferrate(II) ion, while in solutions with lower concentrations of oxalate ion, the dioxalatoferrate(II) ion is the reduction product. By measuring the concentration of dissolved trioxalatoferrate(III) ion that exists in equilibrium with precipitated iron(III) hydroxide in solutions of known pH and known oxalate ion concentration, the dissociation constant of the iron(III) complex was calculated to be 1.0×10^{-18}. Combining this value with the ratios of the dissociation constants of the oxidized to the reduced complex ions, which were obtained from the polarographic data, the dissociation constant of the trioxalatoferrate (II) ion was found to be 6.1×10^{-6}, and that of the dioxalatoferrate(II) ion was 2.7×10^{-5}. The half-wave potential in one molar potassium oxalate solution was found to be -0.25_7 volts (vs. S.C.E.), which is an approximation of the standard electrode potential. The diffusion current constant, $I = i_d/Cm^{\frac{2}{3}} t^{\frac{1}{6}}$, was measured to be 1.54 ± 0.04 microamps.millimoles^{-1} liter mg.$^{-\frac{2}{3}}$ sec.$^{\frac{1}{2}}$ for the trioxalatoferrate(III) ion in solutions of ionic strength 0.5.

Comparison of the half-wave potentials obtained experimentally in acidic oxalate solutions with those calculated theoretically, taking into account the variation of the mol fraction of the divalent oxalate anion with pH, indicated that even in solutions where the concentration of the monohydrogen oxalate ion is in great excess over that of the divalent oxalate anion, the divalent anion remains the complexing agent.

These results substantiate the polarographic findings of Lingane (2,3), with regard to the oxalato complexes, rather than those of Stackelberg and Freyhold (4) or those of Toropova (5). Lingane obtained evidence for the same iron (II) and iron(III) complexes and gave similar values for their dissociation constants. Stackelberg and Freyhold reported that the half-wave potentials remained constant in solutions containing from 0.01 to 1.0 molar oxalate ion, thus indicating that the trioxalatoferrate(II) ion is the only reduction product over that concentration range. The dissociation constants reported by Toropova differ greatly from those obtained here.

Polarographically reversible, one-electron reduction waves were observed for the reduction of iron(III) in 0.02 to 3.0 molar potassium malonate solutions. By measuring the concentration of the dissolved iron(III) complex as a function of malonate concentration and pH in the presence of precipitated iron(III) hydroxide, it was concluded that the iron(III) complex is trimalonatoferrate(III) ion, having a dissociation constant of 2.2×10^{-16}.

In solutions containing more than 0.3 molar potassium malonate, the variation of the half-wave potentials as a function of malonate ion concentration corresponded quite closely to that predicated for a reduction proceeding from the trimalonatoferrate(III) ion to the dimalonatoferrate(II) complex ion. The dissociation constant of this iron(II) complex was calculated to be 6.5×10^{-3}. At malonate concentrations less than 0.3 molar, the polarographic data do not closely cor-

respond to an integral difference in the number of malonate groups attached to the iron(II) and iron(III) ions. Of the possible explanations for this result, the most plausible appears to be that the reduction actually proceeds from the trimalonatoferrate(III) ion to undissociated iron(II) malonate molecules, $[Fe\ C_3H_2O_4]^\circ$, and that the assumption that the ratio of the diffusion coefficients and the ratio of the activity coefficients of the oxidized and reduced species remain constant with changing potassium malonate concentration is not valid in this case where the iron(III) complex is a triply charged ion and the iron(II) complex is uncharged.

In the more concentrated malonate solutions, the diffusion current constant observed for the trimalonatoferrate(III) ion fell considerably below the value of 1.44 found for this ion in solutions having an ionic strength of 0.5. The change in the viscosity of the solution with increasing potassium malonate concentration was proposed to account for this diminished rate of diffusion. The equation

$$I\ \eta_w = (\text{Constant})$$

was found to hold for these data over a wide range of concentration. In this equation, I is the diffusion current constant and η_w is the viscosity of the potassium malonate solution measured relative to water.

The polarographic reduction of iron(III) in solutions containing from 0.1 to 4.0 molar potassium succinate was also studied. Since it appeared probable that both succinate and hydroxide ions are involved in the complex, the solutions were prepared so that the variation of the half-wave potential with respect to each of the two complexing anions could be studied independently. In a few of the solutions, the reductions appeared to be reversible, but in most cases where the reversibility test could be applied to the reduction waves, the slopes were somewhat larger than predicted for reversible, one-electron reductions. Accurate application of the reversibility test was not possible when the waves were small due to iron (III) hydroxide precipitation, or when they occured too close

to the anodic mercury dissolution waves. In spite of the failure to establish the reversibility of most of the waves with certainty, some conclusions were drawn from the data on the assumption that the degree of irreversibility is small in most cases and remains approximately constant.

The values of the half-wave potentials in the succinate solutions provided evidence for the existance of several different iron(III) complexes. In the more concentrated succinate solutions which contained no added acid, the half-wave potentials of the colored iron(III) solutions were observed to be about one-half volt negative (vs. S.C.E.) and to show a pH dependence indicative of the presence of at least two hydroxide ions in the iron(III) complex. Addition of sufficient acid to the succinate solutions to decrease the pH to about 5.5 or 6.0 caused the solutions to become colorless and decreased the pH dependence of the half-wave potentials. The reduction waves in these solutions showed half-wave potentials at about zero applied potential, and are probably due to the reduction of a normal and not a basic succinatoferrate(III) complex. Between these extremes in the observed potentials, the data imply the existance of at least one, and perhaps two, additional complexes. Several of the solutions at intermediate pH values gave waves at two different potentials. Such double waves occur if two complexes are simultaneously present in solution and if the equilibrium between them is established slowly.

Comparison of the complexes formed by these three dicarboxylate anions shows that the oxalate and malonate ions form quite similar complexes with both ions of iron. In the case of the succinato complexes, the large and weakly held succinate ions tend to be replaced by hydroxide ions, giving rise to basic complexes. It is probable that the bonding forces in all of these complexes are ionic, since magnetic measurements have shown the presence of five unpaired electrons in the strong trioxalatoferrate(III) complex ion (6).

The order of stability of the complexes with both iron(II) and iron(III) was found to be: oxalato $>$ malonato $>>$ suc-

cinato. A ratio of about two hundred exists between the dissociation constants of corresponding oxalato and malonato complexes, the oxalato complexes with their five-memebred rings being somewhat more stable than the malonato complexes with six-membered rings. A factor of about 10^{14} was found between the complexes of divalent and trivalent iron with the same anion in the case of both the oxalato and malonato complexes. This factor is evidently the result of the differences in size and charge of the two iron ions.

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VITA

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